Inorganic chemistry

Lecturer . 7

<u>Chemical Bonds, Lewis Symbols, and the Octet rule :</u>

Chemical bonding involves mainly the attempt to achieve the rare gas number of valence electrons.

This can be achieved in several ways.

<u>Ionic bond:</u> Electrons are mainly the property of one of the two atoms forming the bond.

<u>Covalent bond:</u> Electrons are shared so that each atom has a noble gas electronic configuration.

<u>Metallic bonds.</u> Electrons are lost into the conduction band.

<u>Ionic Bonding :</u>

This occurs between metallic elements from the left-hand side of the periodic table and non-metallic elements from the right hand side of the periodic table.

$$Na\cdot \; + \; :\ddot{\underset{\cdot\cdot}{Cl}}\cdot \; = \; Na^{+} \; + \; [:\ddot{\underset{\cdot\cdot}{Cl}}:]^{-}$$

Note that Na gives up its lone valence electron to Cl, so that they both end up with an octet of electrons.

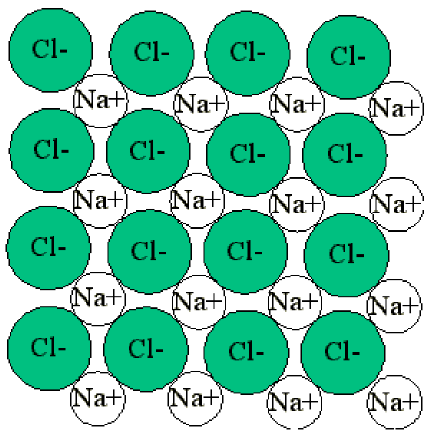
<u>Ionic Bonding</u>

Sodium metal reacts with chlorine gas in a violently exothermic reaction to produce NaCl (composed of Na^{+} and Cl^{-} ions):

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

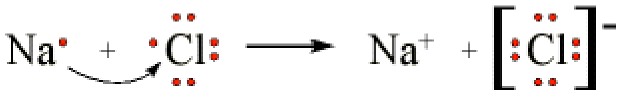
These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):

Slice through a NaCl crystal



The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom.

This can be represented using electron-dot symbols (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an octet of electrons in its valence shell:

Na^+ $2s^2 2p^6$

Cl^- $3s^2 3p^6$

Ionic Compounds

ionic compounds consist of a lattice of positive and negative ions .

Energetics of Ionic Bond Formation

The formation of ionic compounds (like the addition of sodium metal and chlorine gas to form NaCl) are usually *extremely exothermic*.

The loss of an electron from an element:

- **Always *endothermic* (takes energy to strip the e' from the atom)**
- **$Na(g) \rightarrow Na^+(g) + 1e^-$ $\Delta H = 496$ kJ/mol**

The gain of an electron by a nonmetal:

- **Generally *exothermic* (energy released)**
- **$Cl(g) + 1e^- \rightarrow Cl^-(g)$ $\Delta H = -349$ kJ/mol**

The formation of NaCl from Na and Cl would thus *require the input of 147 kJ/mol*. However, it appears to be a highly exothermic reaction.

Ionic compounds are stable due to the *attraction between unlike charges*:

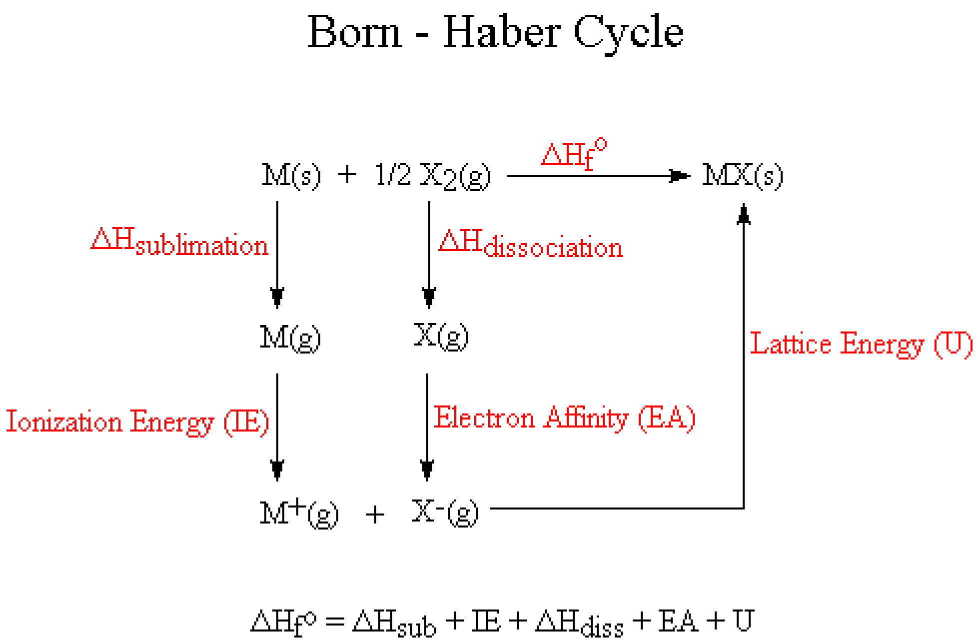
- **The ions are drawn together**
- **Energy is released**
- **Ions form solid *lattice***

Lattice energy:

the energy required to separate completely a mole of a solid ionic compound into its gaseous ions

It is a measure of just how much stabilization results from the arranging of oppositely charged ions in an ionic solid.

The diagram below is the Born-Haber cycle for the formation of an ionic compound from the reaction of an alkali metal (Li, Na, K, Rb, Cs) with a gaseous halogen (F_2, Cl_2). The Born-Haber thermochemical cycle is named after the two German physical chemists, Max Born and Fritz Haber, who first used it in 1919.



The enthalpy change in the formation of an ionic lattice from the gaseous isolated sodium and chloride ions is -788 kJ/mole.

Remember:

The enthalpy or *heat content* (denoted as H or ΔH) is a description of thermodynamic potential of a system, which can be used to calculate the "useful" work obtainable from a closed thermodynamic system under constant pressure.

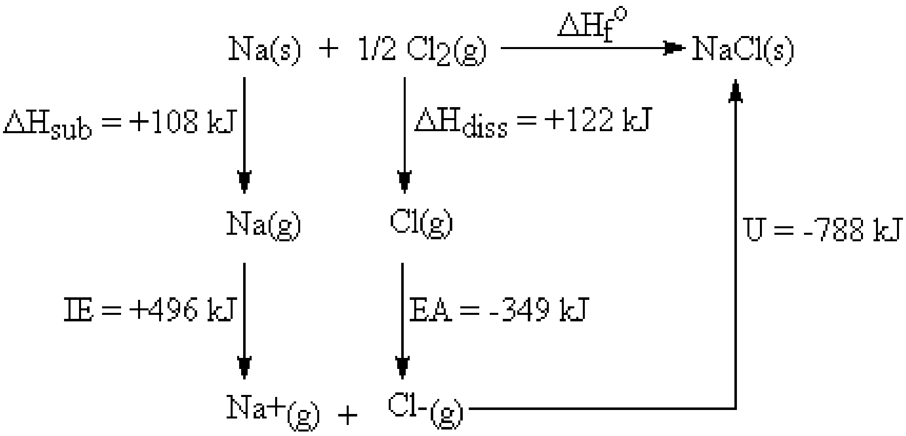
The term *enthalpy* is describing the changes within exo- and endothermic reactions, which minimize at equilibrium.

The lattice energy of an ionic solid is a measure of the strength of bonds in that ionic compound.

- **That enthalpy change, which corresponds to the reaction**
  - **$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$,**
- **is called the lattice energy of the ionic crystal.**
- **Although the lattice energy is not directly measurable, there are various ways to estimate it from theoretical considerations and some experimental values.**
- **For all known ionic crystals, the lattice energy has a large negative value.**

- **It is ultimately the lattice energy of an ionic crystal which is responsible for the formation and stability of ionic crystal structures.**

For sodium chloride, the Born - Haber cycle is:



$$\Delta H_f^\circ = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$$

$$\Delta H_f^\circ = 108 + 496 + 122 - 349 - 788 = -411 \text{ kJ/mole}$$

A cycle of this type is an example of Hess's Law. It can be used to calculate any of the six enthalpies, given the other five.

The magnitude of the lattice energy depends upon the charges of the ions, their size and the particular lattice arrangement.

<u>Sublimation Energies of the Alkali Metals</u>

decrease ↓

Element	Sublimation Energy, kJ/mole
Li	162
Na	108
K	90
Rb	81
Cs	79

<u>Heat of Dissociation (with Heat of Vaporization for Br_2(l) and Heat of Sublimation for I_2(s) added) of the Halogens</u>

Increase ↓

Element	Energy per mole of X, kJ/mole
F_2	79
Cl_2	122
Br_2	112
I_2	107

Example :

Calculate the lattice energy of $MgCl_2$ (S). For Mg, the enthalpy of sublimation is 150 KJ/mol, the first ionization energy is +738 KJ/mol, and the second IE is +1450 KJ/mol. For Cl_2(g), and the first electron affinity is -348 KJ/mol of Cl(g). For $MgCl_2$ (S), the enthalpy of formation is -624 KJ/mol.

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Electron configuration of ions

How does the energy released in lattice formation compare to the energy required to strip away another electron from the Na^+ ion?

Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would take far more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}.

This amount of energy can compensate for values as large as I_3 for valence electrons

(i.e. can strip away up to 3 electrons).

Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core (thus they may have *color*). Some examples which can form a noble gas core (and be colorless):

Ag: $[Kr]5s^1 4d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl

Cd: $[Kr]5s^2 4d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule)

Compound	Lattice Energy (kJ/mol)
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
$SrCl_2$	2130
MgO	3938

Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest principle quantum number

A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell.

Iron will not have a noble gas core (iron salts will have color)

Fe: $[Ar]4s^2 3d^6$ Fe^{2+} $[Ar]\ 3d^6$

Fe: $[Ar]4s^2 3d^6$ Fe^{3+} $[Ar]\ 3d^5$

Polyatomic ions

In polyatomic ions, two or more atoms are bound together by covalent (chemical) bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion.

Basic Concepts of Chemical Bonding Sizes of Ions

Sizes of ions influence:

- ***packing*** **of ions in ionic lattices, and therefore, the** ***lattice energy***
- **biological recognition - some ions can pass through certain membrane channels, others may be too large**

The size of an ion is influenced by:

- **nuclear charge**
- **number of electrons**
- **valence orbitals**

Cations

- **formed by removing one or more valence electrons**
- **vacates the most spatially extended orbitals**
- **decreases the total electron-electron repulsion in the outer orbital**

Cations are therefore smaller than the parent atom

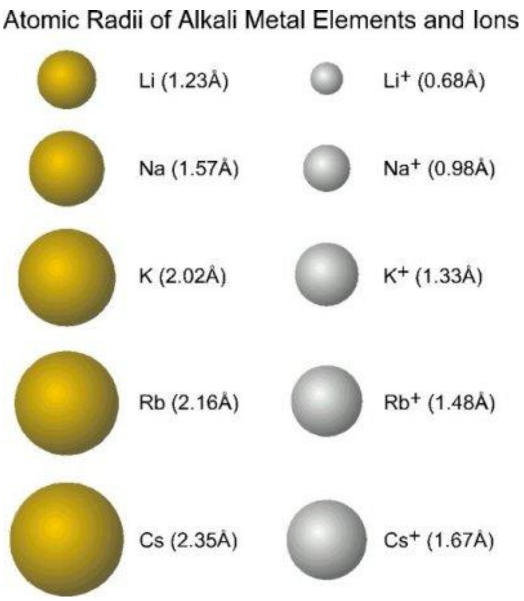
Anions

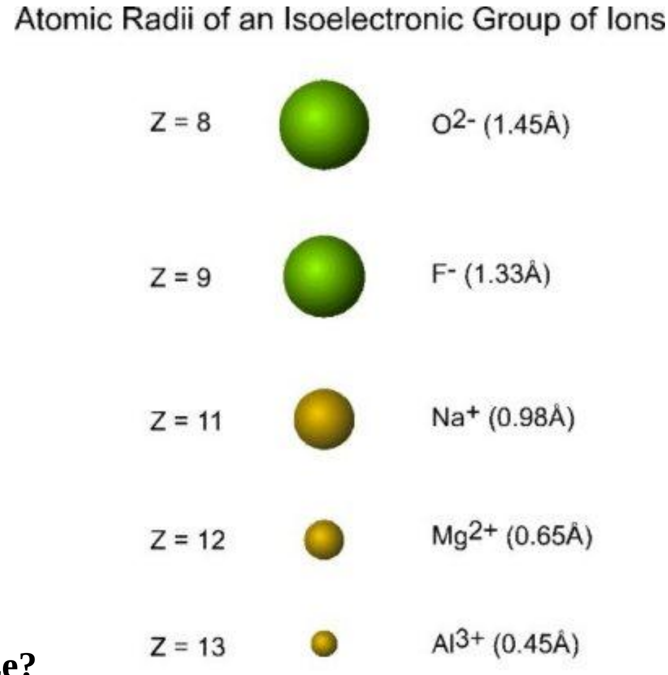
- **formed by addition of one or more valence electrons**
- **fills in the most spacially extended orbitals**
- **increases electron-electron repulsion in outer orbital**

Anions are therefore larger than the parent atom

For ions of the same charge (e.g. in the same group) the size increases as we go down a group in the periodic table

As the principle quantum increases the size of both the parent atom and the ion will increase





How does the nuclear charge affect ion size?

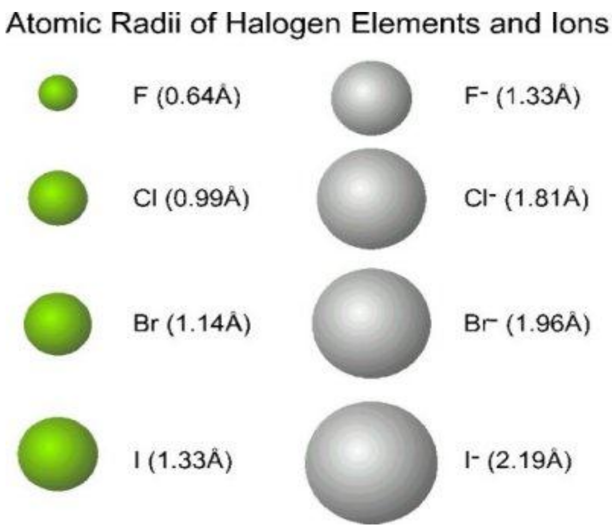
Consider the following collection of ions:

ion	electrons	protons
O^{2-}	10	8
F^{-}	10	9
Na^{+}	10	11
Mg^{2+}	10	12
Al^{3+}	10	13

Each ion:

- **contains the same number of electrons (10; with configuration $1s^2 2s^2 2p^6$) and are thus termed a collection of *isoelectronic* ions**
- **varies in the *nuclear charge***

The radius of each ion decreases with an increase in nuclear charge:



Oxygen and fluorine <u>precede</u> neon and are *nonmetals*, sodium, magnesium and aluminum come <u>after</u> neon and are *metals*.

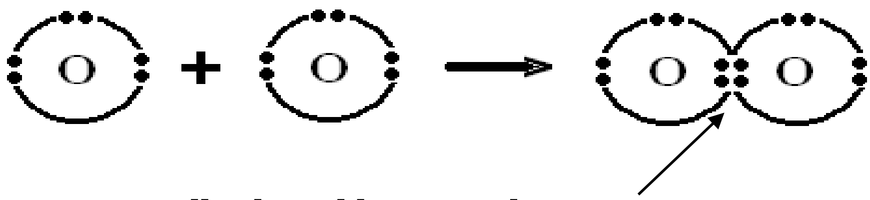
Metals, Nonmetals and Metalloids

Characteristic properties of metallic and non-metallic elements:

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, compounds
Cations in aqueous solution	Anions, oxyanions in aqueous solution

Covalent bonding :

Here the two atoms share the electrons to achieve a covalent bond.



two pairs of electrons equally shared between the two oxygen atoms.

Covalent Bonding

Ionic substances:

- **usually brittle**
- **high melting point**
- **organized into an ordered lattice of atoms, which can be cleaved along a smooth line**

the electrostatic forces organize the ions of ionic substances into a rigid, organized three-dimensional arrangement

<u>The vast majority of chemical substances are *not ionic* in nature</u>

- **gases and liquids, in addition to solids**
- **low melting temperatures**

Lewis Dot Structures (VSEPR)

G. N. Lewis was probably the best chemist who never won the Nobel Prize .

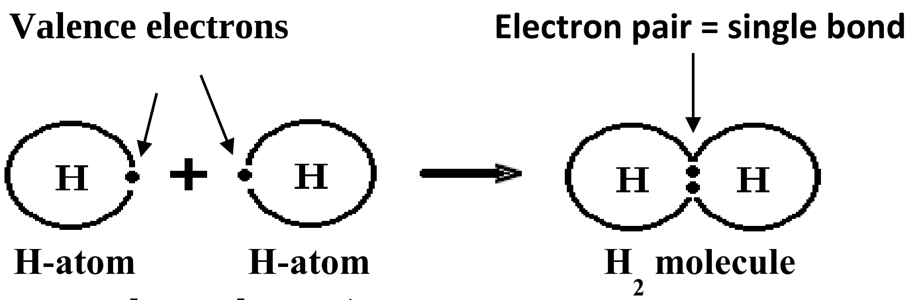
G.N. Lewis

reasoned that an atom might attain a noble gas electron configuration by *sharing* electrons

A chemical bond formed by sharing a pair of electrons is called a covalent bond

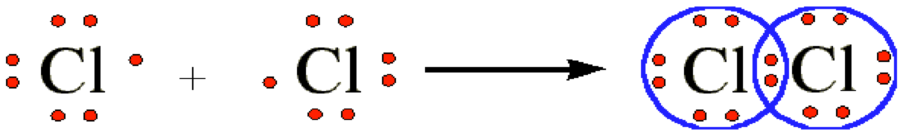
<u>Lewis Dot Structures (revision)</u>

Lewis dot structures present a simple approach to bonding that allows us to rationalize much molecular structure. The idea is that atoms share electrons in the valence shell to form the chemical bond, with one pair of electrons per bond. Note that each H-atom has two electrons, which is the structure of He, the next inert gas.



(Each H-atom has one valence electron)

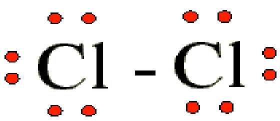
When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:

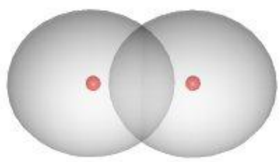


Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon.

In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:

H - H





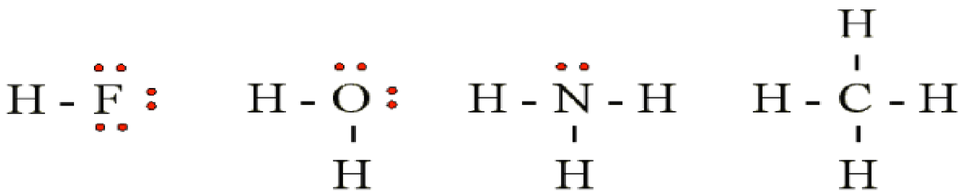
The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:

The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them

For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

Element	Group	Valence electrons	Bonds needed to form valence octet
F	7A	7	1
O	6A	6	2
N	5A	5	3
C	4A	4	4

Examples of hydride compounds of the above elements (covalent bonds with hydrogen:



Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements

Multiple bonds

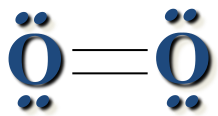
The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a *single bond*

In many molecules atoms attain complete octets by sharing more than one pair of electrons between them.

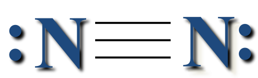
Double and Triple Bonds

Atoms can share four electrons to form a double bond or six electrons to form a triple bond .

O_2 :



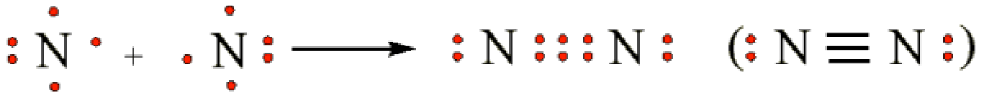
N_2 :



The number of electron pairs is the bond order.

Two electron pairs shared a *double bond*

Three electron pairs shared a *triple bond*



Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet.

- **N_2 is fairly inert, due to the strong triple bond between the two nitrogens**
- **The N - N bond distance in N_2 is 1.10 Å (fairly short)**

From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- **N-N 1.47Å**
- **N=N 1.24Å**
- **N≡N 1.10Å**

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases

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